

an additional 20 g. of perfluoropropene was charged into the autoclave which was heated for 40 hours more at 201°. Seventy grams of olefin and 15 g. of  $\text{CF}_2\text{ClCFClI}$  were recovered. Rectification of the remaining product *in vacuo* gave  $\text{CF}_2\text{ClCFCl}[\text{CF}_2\text{CF}(\text{CF}_3)]_n\text{I}$  where  $n = 1$  (25 g.), b.p. mostly 58.5–60.5° at 20 mm.,  $n_{\text{D}}^{25}$  1.3908,  $\lambda_{\text{max}}$  282  $\mu$ ,  $\epsilon$  203. *Anal.* Calcd. for  $\text{C}_5\text{Cl}_2\text{F}_3\text{I}$ : C, 14.0. Found: C, 14.4, 14.5. Where  $n = 2$  (15 g.), b.p. mostly 97.5–104° at 20 mm.,  $n_{\text{D}}^{25}$  1.3760,  $\lambda_{\text{max}}$  282  $\mu$ ,  $\epsilon$  205. *Anal.* Calcd. for  $\text{C}_9\text{Cl}_2\text{F}_5\text{I}$ : C, 16.6. Found: C, 16.6, 16.9. Where  $n = 3_{\text{av}}$  (7 g.), b.p. mostly 77–87° at ca. 0.1 mm.,  $n_{\text{D}}^{25}$  1.3706 (not analyzed). Where  $n = 4_{\text{av}}$  (4 g.), b.p. 87–138° at ca. 0.1 mm.,  $n_{\text{D}}^{25}$  1.3691,  $\lambda_{\text{max}}$  282  $\mu$ . *Anal.* Calcd. for  $\text{C}_{14}\text{Cl}_2\text{F}_7\text{I}$ : C, 19.1; mol. wt., 879. Found: C, 19.0; mol. wt. (from absorbancy at 282  $\mu$  of a known concentration in 2,3,3-trichloroheptafluorobutane using an  $\epsilon$  value of 205), 850.

**The Thermal Reaction of 1,2-Dichloro-2-iodo-1,1,2-trifluoroethane with Chlorotrifluoroethylene.** (a) **In Autoclaves.**—A 1-l. stainless steel autoclave was charged with 650 g. (2.33 moles) of 1,2-dichloro-2-iodo-1,1,2-trifluoroethane and 248 g. (2.13 moles) of chlorotrifluoroethylene (1:1:1 mole ratio of iodide to olefin) and heated for 5 hr. at 180° in a molten salt-bath. During this time a pressure drop from 500 to 300 p.s.i. was observed with the major portion of the reaction occurring in the first hour ( $\Delta P = 125$  p.s.i.).

Forty-five grams of olefin was recovered from the autoclave by gaseous transfer to a Dry Ice-cooled trap, and the remaining products were distilled through a short Vigreux column. A total of 581 g. of  $\text{CF}_2\text{ClCFClI}$  was recovered, b.p. 99–102°, and telomer fractions,  $\text{CF}_2\text{ClCFCl}(\text{CF}_2\text{CFCl})_n\text{I}$ , were taken as follows:  $n = 1$ –2, b.p. 45–93° at 1 mm. (36 g.);  $n = 3$ –4, b.p. to 150° at <0.1 mm. (80 g.). When the vapor temperature of 150° was reached, the temperature of the still-pot was sufficiently elevated due to the presence of very high molecular weight telomers to cause extensive liberation of iodine and the distillation had to be stopped. The distilled fractions were identified and the composition of the hard waxy residue (127 g.) was estimated to be  $n = 4$  to >20 (mostly  $n > 10$ ) by reference to published physical data<sup>2</sup> and ultraviolet molar extinction determinations.

Another experiment was carried out using a molar ratio of  $\text{CF}_2\text{ClCFClI}:\text{CF}_2=\text{CFCl}$  of 15:1 at 160–170° for 5.7 hr. The yield of  $n = 1$  and 2 was <20%, whereas under liquid phase photochemical conditions (5 days) a 75% yield of  $n = 1$  was obtained by Haszeldine.<sup>2</sup>

(b) **In Hot Tubes.**—An attempt to prepare  $n = 1$  by

passing  $\text{CF}_2=\text{CFCl}$  through a large excess of refluxing  $\text{CF}_2\text{ClCFClI}$  in a vertical column heated to 180° failed to give any significant reaction. Therefore, an alternative reaction system allowing higher pressures and temperatures as well as short contact time was designed.

At an average rate of 9.6 g./min., a mixture of 2230 g. (8.0 moles) of 1,2-dichloro-2-iodo-1,1,2-trifluoroethane and 160 g. (1.37 moles) of chlorotrifluoroethylene was pumped by means of a Lapp Pulsafeeder micropump from a charge cylinder through a stainless steel coil immersed in a molten salt-bath at 200°. Practically all of the coil volume was occupied by liquid phase, and the contact time in this hot zone was calculated as <10 min. During the reaction, the pressure was maintained at 750 p.s.i. by adjusting the rate at which products were vented from the coil to a Dry Ice-cooled receiving gas cylinder. Twelve grams of chlorotrifluoroethylene and 2150 g. of  $\text{CF}_2\text{ClCFClI}$  were recovered. The product distribution of the remaining 211 g. of crude telomer was  $n = 1$  (22%),  $n = 2$  (22%),  $n = 3$  (22%) and  $n = 4$  to >10 (33%).

In the above apparatus at a rate of 17 g./min. at 195–200° and at pressures of 600–650 p.s.i. only slight reaction occurred.

**The Thermal Reaction of 1,2-Dichloro-2-iodo-1,1,2-trifluoroethane with Tetrafluoroethylene.**—1,2-Dichloro-2-iodo-1,1,2-trifluoroethane (200 g., 0.716 mole) and 30 g. (0.316 mole) of tetrafluoroethylene (2.4 mole ratio of iodide to olefin) were charged into a 300-ml. nickel autoclave and heated in a molten salt-bath for 2.75 hr. at 171°. After the reaction period, during which the pressure fell from 600 to 450 p.s.i., 15 g. of tetrafluoroethylene was recovered. From the remaining products 170 g. of  $\text{CF}_2\text{ClCFClI}$  was recovered (some handling losses), and 16 g. of a white crumbly solid was the only other product. This solid contained only very small amounts of iodine and its ultraviolet spectrum showed a very faint maximum at ca. 270  $\mu$ . Its infrared spectrum closely resembled that of polytetrafluoroethylene.

**Ultraviolet Spectra.**—A Beckman ratio recording spectrophotometer, model DK-2, was used.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE STATE UNIVERSITY]

## Studies in Organic Sulfur Compounds. IX.<sup>1</sup> Preparation and Desulfurization of Optically Active 1,1-Diphenyl-3-mercaptopropan-2-ol<sup>2</sup>

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Acid cleavage of spiro-(5-diphenylmethyl-1,3-oxathiolane-2,3'-cholestane) (I) followed by lithium aluminum hydride reduction of the resulting disulfide VII led to optically pure 1,1-diphenyl-3-mercaptopropan-2-ol (IV). Raney nickel desulfurization of this  $\beta$ -mercaptoethanol or of its O,S-dibenzoate (VI) furnished 1,1-diphenylpropan-2-ol or its benzoate, respectively. The rotations of this alcohol (IIIa) and its derivatives were identical with those of the earlier prepared desulfurization product of the hemithioketal I. These results show that no racemization occurs in the formation of alcohols by Raney nickel desulfurization of hemithioketals (e.g., I) or of  $\beta$ -mercaptoethanols (e.g., IV).

The observation<sup>1</sup> that Raney nickel desulfurization of hemithioketals (1,3-oxathiolanes) results in introduction of oxygen has led to an investigation of the scope of this reaction, and the appropriate experiments will be reported at a future time. We have also been concerned with the mechanism of this reaction and certain observations bearing

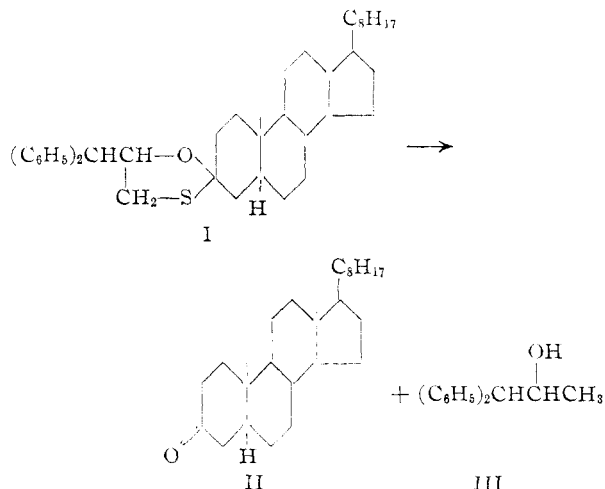
(1) Paper VIII, C. Djerassi, M. Gorman and J. A. Henry, *THIS JOURNAL*, **77**, 4647 (1955).

(2) This work was carried out under contract No. DA-20-018-ORD-13474 with the Office of Ordnance Research, U. S. Army.

on this aspect form the subject of the present paper.

The desulfurization of spiro-(5-diphenylmethyl-1,3-oxathiolane-2,3'-cholestane) (I) led<sup>1</sup> to over 50% each of cholestan-3-one (II) and 1,1-diphenylpropan-2-ol (III). This alcohol (III) was optically active ( $[\alpha]_{\text{D}} +5.8^\circ$ , 3,5-dinitrobenzoate  $[\alpha]_{\text{D}} -46.8^\circ$ ), and since an antipode with the same optical properties (but opposite in sign) was isolated by desulfurization of a diastereoisomer of the hemithioketal I, it was assumed that complete re-

tention of optical activity is observed in this reaction. This leads to the mechanistically important conclusion that the oxygen present in the original hemithioketal I is the one eventually found in 1,1-diphenylpropan-2-ol (III) and that rupture of the C-O bond during the desulfurization occurred only at the position indicated by the dotted line<sup>3</sup> in structure I.

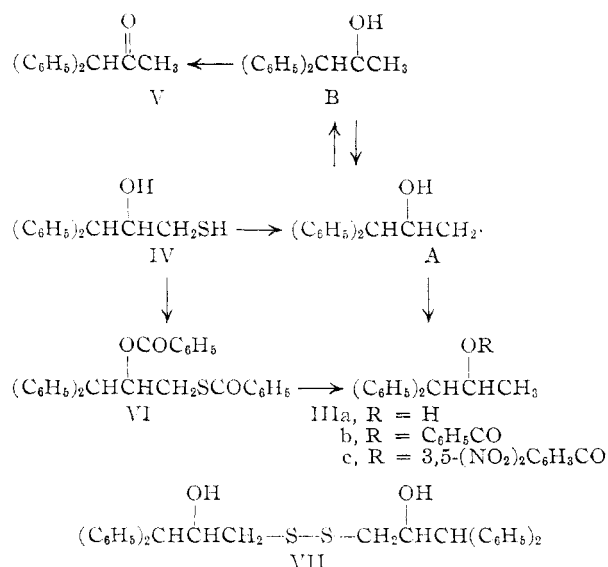


The fact that both antipodes of 1,1-diphenylpropan-2-ol (III) were obtained does not exclude rigorously the possibility that partial racemization to *exactly the same extent* may have occurred in the desulfurization of the two diastereoisomeric hemithioketals (I), and independent confirmation was considered necessary since optically pure 1,1-diphenylpropan-2-ol (III) has not been described in the literature.<sup>3a</sup> The approach used in the present investigation also has a bearing on the mechanism of the desulfurization of  $\beta$ -mercaptoethanols, since it has been observed earlier<sup>1</sup> that desulfurization will yield a mixture of alcohol (predominant) and ketone. In the case of 1,1-diphenyl-3-mercaptoethanol (IV), both 1,1-diphenylpropan-2-ol (IIIa) and 1,1-diphenylacetone (V) were produced, and it could be demonstrated that they were not formed from each other by reduction or oxidation. Mechanistically, two simple paths can be suggested for the formation of the alcohol and these are not mutually exclusive: (a) the initially formed free radical A may pick up hydrogen to lead directly to the alcohol IIIa or (b) there may occur a 1,2-shift to the radical B which could either lose a hydrogen atom to give the ketone V or accept one, thus providing an alternate route to the alcohol IIIa.

Experimentally, these two mechanisms should be differentiable by studying the desulfurization of an optically active  $\beta$ -mercaptoethanol since only intermediate B would involve racemization. It was felt that by preparing optically active 1,1-diphenyl-3-mercaptoethanol (IV) both ques-

(3) This is based on the assumption that complete retention of configuration rather than complete inversion of configuration is involved in the desulfurization of the hemithioketal.

(3a) NOTE ADDED IN PROOF.—It has been called to our attention that both antipodes of this alcohol and certain of its derivatives have been described already by D. J. Cram and F. A. Abd Elhafez, *THIS JOURNAL*, **76**, 28 (1954).



tions posed above could be answered in a satisfactory manner.

Since hemithioketals can be cleaved by means of acid,<sup>4</sup> the three diastereoisomeric hemithioketals I<sup>1</sup> constituted an ideal starting material for the preparation of an optically pure  $\beta$ -mercaptoethanol, which had the additional advantage of being crystalline. Treatment of any one of the three diastereoisomeric hemithioketals I<sup>1</sup> with hydrochloric acid in boiling *unpurified* dioxane yielded the same crystalline product, m.p. 140–142°, which was shown to be bis-(1,1-diphenyl-2-hydroxy-3-propyl) disulfide (VII).<sup>5</sup> Diastereoisomers B and C<sup>1</sup> yielded levorotatory material ( $[\alpha]_D - 168^\circ$ ) while diastereoisomer A<sup>1</sup> furnished the dextrorotatory antipode ( $[\alpha]_D + 170^\circ$ ). Reduction of the appropriate disulfide VII with lithium aluminum hydride afforded the two optically pure antipodes of crystalline 1,1-diphenyl-3-mercaptoethanol (IV),<sup>6</sup> further characterized as the O,S-dibenzoate VI. The alcohol IV could be obtained directly from the hemithioketal I when the acid cleavage was conducted in *freshly purified* dioxane, suggesting that peroxides in the unpurified solvent were responsible for disulfide formation.

Raney nickel desulfurization of (+)-1,1-diphenyl-3-mercaptoethanol (IV) yielded 1,1-diphenylacetone (V) and 1,1-diphenylpropan-2-ol (IIIa) identical in all respects including rotation of the alcohol and its 3,5-dinitrobenzoate (IIIc) with specimens obtained earlier<sup>1</sup> by desulfurization of diastereoisomer A of the hemithioketal I. Furthermore, desulfurization of the O,S-dibenzoate VI<sup>7</sup> led to an optically active benzoate IIIb which had the same rotation as the benzylation product of 1,1-diphenylpropan-2-ol obtained by desul-

(4) J. Romo, G. Rosenkranz and C. Djerassi, *ibid.*, **73**, 4961 (1951).

(5) A control experiment with *dl*-1,1-diphenyl-3-mercaptoethanol (IV) demonstrated that it was converted into the disulfide VII when subjected to the same treatment as the hemithioketal I.

(6) The racemic substance already has been prepared by another procedure by C. Djerassi, M. Gorman, F. X. Markley and E. B. Oldenburg, *THIS JOURNAL*, **77**, 568 (1955).

(7) It is pertinent to note that no diphenylacetone (V) was encountered in this experiment.

furization of either I or IV. On the basis of these results, we feel confident that the earlier assumed<sup>1</sup> retention of optical activity in the desulfurization of hemithioketals (such as I) is indeed justified and that the desulfurization of  $\beta$ -mercaptoethanols (such as IV) to the corresponding alcohol (such as III) does not involve the carbon atom bearing the alcoholic function.

### Experimental<sup>8</sup>

**Bis-(1,1-diphenyl-2-hydroxy-3-propyl) Disulfide (VII).**—A mixture of 1.5 g. of isomer C (m.p. 153°) of spiro-(5-diphenylmethyl-1,3-oxathiolane-2,3'-cholestane) (I),<sup>1</sup> 100 cc. of *unpurified* dioxane, 8 cc. of concd. hydrochloric acid and 20 cc. of water was heated under reflux for 18 hr., cooled, diluted with water and extracted with ether. The washed and dried ethereal solution was evaporated to dryness and the residue was chromatographed on 50 g. of Fisher alumina deactivated in hexane solution with 5 cc. of 10% acetic acid. Elution with hexane gave 210 mg. of recovered hemithioacetal I while 620 mg. of cholestan-3-one (II) (m.p. 127–129°) was eluted with 8:2 hexane-benzene. The desired disulfide (380 mg.) was eluted with 1:1 hexane-benzene and after two recrystallizations from hexane-ether yielded 320 mg. of colorless crystals, m.p. 140–142°,  $[\alpha]_D^{25} -168^\circ$  (*c* 0.55).

*Anal.* Calcd. for  $C_{30}H_{30}O_2S_2$ : C, 74.05; H, 6.22; S, 13.16; mol. wt., 486. Found: C, 74.40; H, 6.20; S, 13.26; Rast mol. wt., 438.

Similar cleavage of 2.0 g. of isomer A (m.p. 194°) yielded 0.42 g. of (+)-bis-(1,1-diphenyl-2-hydroxy-3-propyl) disulfide, m.p. 140–142°,  $[\alpha]_D^{25} +170^\circ$  (*c* 0.6), while 1.1 g. of isomer B (m.p. 175°) gave 0.2 g. of the (–)-disulfide VII.<sup>4</sup>

The *dl*-disulfide, m.p. 110–112°, was prepared by boiling *dl*-1,1-diphenyl-3-mercaptopropan-2-ol (IV)<sup>6</sup> with unpurified dioxane-hydrochloric acid for 24 hr.

**1,1-Diphenyl-3-mercaptopropan-2-ol (IV).** (a) *By Acid Cleavage in Purified Dioxane of Spiro-(5-diphenylmethyl-1,3-oxathiolane-2,3'-cholestane) (I).*—A solution of 4.0 g. of isomer A<sup>1</sup> of the hemithioacetal I was heated under reflux for 24 hr. in 200 cc. of freshly purified (distilled from sodium) dioxane with 16 cc. of concd. hydrochloric acid and 40 cc. of water. The mixture was processed as above and after separating much unreacted hemithioacetal and some cholestan-3-one, 280 mg. of the desired (+)-1,1-diphenyl-3-mercaptopropan-2-ol (IV) was obtained from the hexane-benzene (1:1) eluates; m.p. 69–72°, raised after recrystallization from hexane-ether to m.p. 74–75°,  $[\alpha]_D^{25} +38^\circ$  (*c* 1.05). The antipode ( $[\alpha]_D^{25} -36^\circ$ ) was obtained in the same manner from isomer C.

*Anal.* Calcd. for  $C_{15}H_{16}OS$ : C, 73.75; H, 6.60. Found: C, 73.29; H, 6.88.

(b) *By Lithium Aluminum Hydride Reduction of Bis-(1,1-diphenyl-2-hydroxy-3-propyl) Disulfide (VII).*—A solution of 300 mg. of the (–)-disulfide VII in 50 cc. of tetra-

hydrofuran was heated under reflux for 24 hr. with a large excess of lithium aluminum hydride. Decomposition of the reagent with ethyl acetate followed by addition of 10% hydrochloric acid and isolation with ether yielded 280 mg. of the above described (–)-1,1-diphenyl-3-mercaptopropanol, m.p. 70–74°, which was raised to 74–75° after one recrystallization. Similar treatment of 100 mg. of the (+)-disulfide VII gave 80 mg. of (+)-1,1-diphenyl-3-mercaptopropan-2-ol (IV).

**1,1-Diphenyl-3-mercaptopropan-2-ol O,S-Dibenzoate (VI).**—A mixture of 200 mg. of (+)-1,1-diphenyl-3-mercaptopropan-2-ol (IV), 1 cc. of benzoyl chloride and 5 cc. of pyridine was allowed to stand at room temperature for 24 hr., diluted with water, and the product was extracted with ether. After appropriate washing and drying, the residue was recrystallized from methanol to furnish 230 mg. of the (+)-dibenzoate, m.p. 129–131°,  $[\alpha]_D^{25} +69^\circ$  (*c* 0.70);  $\lambda_{max}^{CHCl_3}$  5.76, 5.93, 7.82, 8.43 and 8.95  $\mu$ .

*Anal.* Calcd. for  $C_{29}H_{24}O_3S$ : C, 76.97; H, 5.35; S, 7.07. Found: C, 76.91; H, 5.45; S, 6.80.

Similar treatment of the *dl*-mercaptopropanol<sup>6</sup> yielded *dl*-1,1-diphenyl-3-mercaptopropan-2-ol dibenzoate (VI), m.p. 146–147°, the infrared spectrum (chloroform solution) of which was identical with that of the (+)-isomer.

*Anal.* Found: C, 77.45; H, 5.44; S, 6.81.

**Desulfurization of 1,1-Diphenyl-3-mercaptopropan-2-ol (IV).**—A 350-mg. sample of (+)-1,1-diphenyl-3-mercaptopropan-2-ol in 100 cc. of ethyl methyl ketone was heated with stirring under reflux with 6 g. of 3 day old W-2 Raney nickel catalyst (deactivated by heating for 1 hr. in ethyl methyl ketone solution). The reaction mixture was processed in the previously described manner<sup>1</sup> including chromatography. Elution with hexane gave 65 mg. of diphenylacetone (V), m.p. 55–58° (identified by infrared spectrum), while the desired diphenylpropanol (IIIa)<sup>1</sup> (150 mg., m.p. 56–58°,  $[\alpha]_D^{25} +6^\circ$ ) was removed with 1:1 hexane-benzene. The alcohol was converted into (+)-1,1-diphenylpropan-2-ol 3,5-dinitrobenzoate (IIIC)<sup>1</sup> which exhibited m.p. 154–155°,  $[\alpha]_D^{25} -44.4^\circ$  (*c* 0.95) after recrystallization from methanol, and into (+)-1,1-diphenylpropan-2-ol benzoate, m.p. 78–79°,  $[\alpha]_D^{25} +18^\circ$  (*c* 2.03).

**Desulfurization of 1,1-Diphenyl-3-mercaptopropan-2-ol O,S-Dibenzoate (VI).**—The desulfurization of 300 mg. of *dl*-1,1-diphenyl-3-mercaptopropan-2-ol O,S-dibenzoate was carried out in the above described manner with 6 g. of 4 day old W-2 Raney nickel catalyst in 100 cc. of ethyl methyl ketone for 2 days. Recrystallization of the crude reaction product yielded 120 mg. of *dl*-1,1-diphenylpropan-2-ol benzoate (m.p. 90–92°). In order to ensure the absence of 1,1-diphenylacetone in the mother liquors, these were saponified with 10% methanolic potassium hydroxide solution, and the total product was found not to possess any carbonyl band in the infrared. Chromatography yielded 55 mg. of 1,1-diphenylpropan-2-ol, m.p. 59–61°.

When the desulfurization was carried out with (–)-1,1-diphenyl-3-mercaptopropan-2-ol O,S-dibenzoate, there was obtained after recrystallization from methanol (–)-1,1-diphenylpropan-2-ol benzoate (IIIb), m.p. 77–79°,  $[\alpha]_D^{25} -17^\circ$  (*c* 0.43), the infrared spectrum of which was identical with that of the *dl*-benzoate.

*Anal.* Calcd. for  $C_{22}H_{20}O_2$ : C, 83.51; H, 6.37. Found: C, 83.52; H, 6.54.

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(8) All melting points were determined on the Kofler block. We are indebted to Mrs. Dolores Phillips for the infrared spectral measurements and to Dr. A. Bernhardt (Mülheim, Germany) for the microanalyses. All rotations were measured in chloroform solution in 1-dm. tubes.